

Chemical shift of Mn and Cr K-edges in X-ray absorption spectroscopy with synchrotron radiation

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Abstract. Mn and Cr K X-ray absorption edges were measured in various compounds containing Mn in Mn²⁺, Mn³⁺ and Mn⁴⁺ oxidation states and Cr in Cr³⁺ and Cr⁶⁺ oxidation states. Few compounds possess tetrahedral coordination in the 1st shell surrounding the cation while others possess octahedral coordination. Measurements have been carried out at the energy dispersive EXAFS beamline at INDUS-2 Synchrotron Radiation Source at Raja Ramanna Centre for Advanced Technology, Indore. Energy shifts of ~8–16 eV were observed for Mn K edge in the Mn-compounds while a shift of 13–20 eV was observed for Cr K edge in Cr-compounds compared to values in elemental Mn and Cr, respectively. The different chemical shifts observed for compounds having the same oxidation state of the cation but different anions or ligands show the effect of different chemical environments surrounding the cations in determining their X-ray absorption edges in the above compounds. The above chemical effect has been quantitatively described by determining the effective charges on Mn and Cr cations in the above compounds.

Keywords. Mn K edge; Cr K edge; EXAFS; synchrotron radiation; energy shift; oxidation state; effective charge.

1. Introduction

It is well known that the X-ray absorption edge of a metal atom changes from its elemental state when it takes part in the formation of a compound. Generally, the absorption edge shifts to higher energy as the core electron binding energy increases, since the metal atom transforms to a positive ion while participating in the formation of a chemical bond and this energy shift (ΔE) increases with an increase in the oxidation state or positive charge on the metal ions. Thus, as the valency or oxidation state of the metal increases, the absorption edge ideally should shift towards higher value. However, as many researchers have observed (Nigam and Gupta 1974; Kondawar and Mande 1976; Ballal and Mande 1977; Apte and Mande 1981; Chetal *et al* 1988; Pandey *et al* 1990; Hinge *et al* 2011; Joseph *et al* 2012), even at the same oxidation state, the absorption edge shifts to different extents depending on several other factors viz. nature of the ligands to the metal ion, coordination numbers, covalent character of the bond, electronegativity of the anion etc or in other words, the chemical environment of the metal ion. The change in absorption edge which could be attributed to different chemical environments of a metal ion having same oxidation state is generally known as chemical effect.

In the present study, we have investigated the chemical effect in different compounds of Mn viz. MnCl₂, MnCO₃, MnSO₄·H₂O, Mn₂O₃, CaMnO₃ and MnO₂, where Mn is

present in different oxidation states (2⁺, 3⁺ and 4⁺ states) and in different compounds of Cr viz. CrCl₃·6H₂O, Cr₂O₃, Cr(SO₄)₃, Cr₂(NO₃)₃·3H₂O, K₂Cr₂O₇ and K₂CrO₄ in which Cr is present in 3⁺ and 6⁺ oxidation states. The study has been carried out by measuring the K X-ray absorption edges of Mn and Cr in the above compounds in a dispersive X-ray absorption spectroscopy beamline at INDUS-2 Synchrotron Radiation Source. It should be noted that most of the earlier studies on chemical shifts of X-ray absorption edges, particularly on Mn and Cr compounds (Ghatikar *et al* 1977; Padalia and Nayak 1977; Manthiram *et al* 1980; Mande and Apte 1981) reported in the literature, are based on the data obtained by laboratory EXAFS measurements using weak conventional X-ray sources and hence may lack reliability.

2. Experimental

Samples of appropriate weight, estimated to obtain a reasonable edge jump were collected in powder form and mixed thoroughly with cellulose powder to obtain total weight of 100 mg, and homogenous pellets of 15 mm diameter were prepared using an electrically operated hydraulic press. X-ray absorption spectroscopy measurements near the absorption edges (viz. XANES measurements) were carried out at the dispersive EXAFS beamline (BL-8) in transmission mode at the INDUS-2 Synchrotron Source (2.0 GeV, 100 mA) at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India (Bhattacharyya *et al* 2009; Gaur *et al* 2011; Basu *et al* 2012a, b). The beamline used a

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460-mm long Si (111) crystal having $2d$ value equal to 6.2709 \AA mounted on an elliptical bender, which could bend the crystal to take the shape of an ellipse such that the synchrotron source and the sample position were at the two foci of the ellipse. The crystal was first set in such a fashion that the central portion makes the proper Bragg angle (θ_0) w.r.t. the incident beam and it selected the energy (E_0) corresponding to the absorption edge of interest. Due to the divergent nature of the synchrotron beam, the angle of incidence varied from $(\theta_0 - \Delta\theta)$ at one end of the crystal to $(\theta_0 + \Delta\theta)$ at the other end and hence a band of energy of $E_0 \pm \Delta E$ was selected by the crystal and the whole band simultaneously fell on the sample due to the elliptical bending of the crystal. The elliptical optics offered minimum aberration. Radiation transmitted through the sample got defocused, spatially dispersed and was subsequently detected by a position-sensitive CCD detector having 2048×2048 pixels. The plot of absorption vs photon energy was obtained by recording the intensities I_0 and I_T , as the CCD outputs, without and with the sample, respectively and the absorption coefficient, μ , was obtained using the relation:

$$I_T = I_0 e^{-\mu x}, \quad (1)$$

where x is the thickness of the absorber. Thus, using the above beamline, the full EXAFS spectrum of the sample at any specified absorption edge can be obtained as a single shot within a time frame of 300 ms.

For the present measurements, the Si (111) crystal was set at a proper Bragg angle to obtain a band of energy around 6539 eV for the XANES measurement at Mn edge (around 5989 eV for Cr K-edge XANES measurements). L3 absorption edge of Sm using a pellet of commercially available powder of Sm_2O_3 and K absorption edge of Mn using standard foil of Mn were measured under the same setting of goniometer and crystal bender to calibrate the CCD channels for XANES measurements of Mn compounds. Calibration of CCD channels in case of Cr compounds was done by measuring L3 absorption edges of Pr and Nd using pellets of commercially available Pr_2O_3 and Nd_2O_3 powders.

It should be noted here that the present measurements were carried out with synchrotron radiation as source unlike the other results reported in the reference list where much weaker laboratory sources were used. For each sample, at least 200 spectra were recorded and average was taken to have better accuracy in the data. This has been possible due to the high flux of synchrotron radiation and very fast read out time of the CCD (300 ms) detector used in the present measurement. It should also be mentioned here that, generally in the normal operation of the beamline, an energy resolution of $\sim 1 \text{ eV}$ at 9 keV ($E/\Delta E \sim 10^4$) was achieved, when a spatially dispersed band of 1 keV fell on the 2000 pixels of CCD detector. However, in case of the present measurements, since we are only concerned with the XANES part (portion close to the absorption edge), the goniometer was positioned in such a way that a smaller band of 150 eV fell on CCD spreading over its 2000 pixels and hence a much better energy resolution was obtained ($\sim 0.1 \text{ eV}$).

3. Results and discussion

Figure 1 shows experimental XANES spectra (μ vs energy plots) at Mn K-edge in different Mn samples viz. Mn metal, MnCl_2 , MnCO_3 , $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, Mn_2O_3 , CaMnO_3 and MnO_2 . It can be seen from figure 1 that for almost all the Mn compounds, one strong pre-edge peak is observed in their respective absorption spectrum, because of transition corresponding to metal $1s$ orbital to metal oxide $d-p$ hybridized orbital. This feature is a characteristic of tetrahedral and/or distorted octahedral coordination (Apte and Mande 1981) of the metal cation, while a lack of pre-edge bump in MnCl_2 is possibly because of a perfect octahedral coordination (Nietubyc *et al* 2001). The K edge positions in different samples are obtained by finding out the 1st peak in the 1st derivative of the μ vs energy plot near the edge. The chemical shift values (ΔE) for all the samples are listed in table 1. There are wide variations in the edge shift in Mn compounds measured by different researchers (Ghatikar *et al* 1977; Mande and Apte 1981; Basu *et al* 2012a, b) and our result being closer to that of Ghatikar *et al* (1977).

Figure 2 shows K-edge XANES spectra (μ vs energy plots) for Cr compounds ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, Cr_2O_3 , $\text{Cr}(\text{SO}_4)_3$, $\text{Cr}_2(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, $\text{K}_2\text{Cr}_2\text{O}_7$ and K_2CrO_4). In this case also, for compounds like $\text{K}_2\text{Cr}_2\text{O}_7$ and K_2CrO_4 , where Cr is present in Cr^{6+} oxidation state and having tetrahedral coordination, large pre-edge feature appears in their respective absorption spectrum at 5996.5 eV, which is a characteristic of $1s$ to $3d$ orbital transition (Peterson *et al* 1997; Huggins *et al* 1999; Najih and Huffman 1999; Shaffer *et al* 2001; Dokken *et al* 2007; Parson *et al* 2007). However, the pre-edge

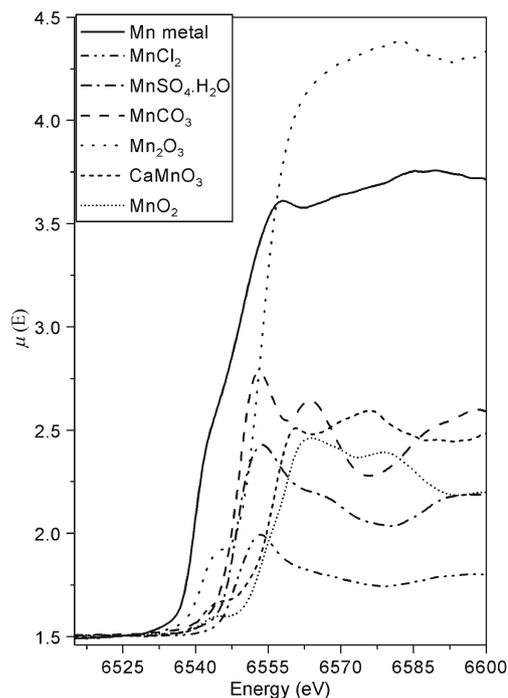
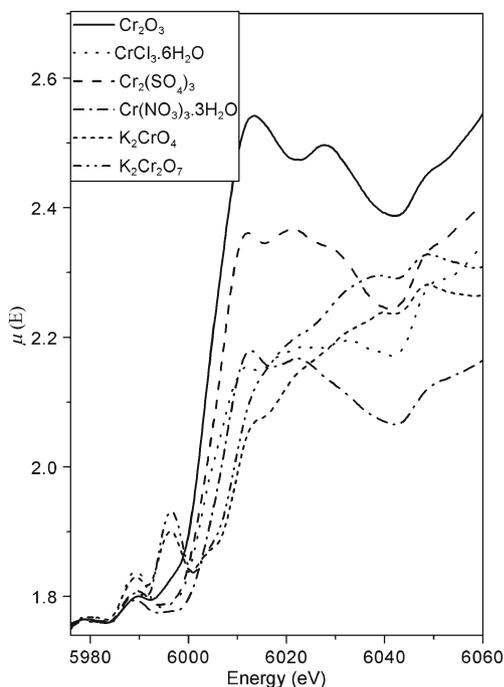


Figure 1. XANES spectra of different Mn compounds around Mn K edge.

Table 1. Chemical shift of Manganese K edge and the estimated effective charge on the manganese ion in the compounds.

Compound	Mn ion oxidation state	Chemical shift (ΔE) (eV)	Effective charge (q)	
			Suchet's formula	Pauling's formula
MnCl ₂	2+	8.17 ± 0.1	1.18	1.66
MnSO ₄ ·H ₂ O*	2+	8.40 ± 0.1	1.22	1.69
MnCO ₃ *	2+	9.30 ± 0.1	1.35	1.83
Mn ₂ O ₃	3+	13.62 ± 0.1	1.87	2.38
MnO ₂	4+	18.83 ± 0.1	2.37	2.92
CaMnO ₃	4+	16.33 ± 0.1	Method 1	1.87
			Method 2	
CaMnO ₃ *	4+	16.33 ± 0.1	2.37	2.92
			2.15	2.67

*Effective charge calculated from the calibration curve of ΔE vs q .

**Figure 2.** XANES spectra of different Cr compounds around Cr K edge.

features are very weak for the compounds where Cr is present in Cr³⁺ oxidation state and having octahedral coordination, viz. in CrCl₃·6H₂O, Cr₂O₃, Cr(SO₄)₃ and Cr₂(NO₃)₃·3H₂O, since 1s to 3d transition is forbidden in octahedral compounds. Edge shifts for all the compounds are calculated at the maximum of first derivative of edge. Chemical shift values for all the Cr compounds are shown in table 2. Edge shifts obtained in some Cr compounds agree well with the result obtained by Manthiram *et al* (1980).

As discussed in the 'Introduction' section, chemical environment around the central absorbing atom such as electronegativity of anions, coordination numbers, oxidation state etc determine the shift in absorption edges of the atom.

Various studies (Nigam and Gupta 1974; Kondawar and Mande 1976; Ballal and Mande 1977; Apte and Mande 1981; Chetal *et al* 1988; Pandey *et al* 1990; Hinge *et al* 2011; Joseph *et al* 2012) have shown that this combined effect of chemical environment can be quantitatively presented by the quantity 'effective charge' (q). Formation of chemical bond in a compound involves redistribution of valence electrons of the constituent atoms and effective charge is a hypothetical parameter which gives a measure of the charge residing over the cation when it forms a bond with a ligand. Apart from the valency, it takes care of the electronegativity of the pair of atoms forming the bond, covalent nature of the bond, coordination number etc and thus quantitatively takes care of the chemical environment around the absorbing metal ions.

Several empirical relations have been proposed in the literature to estimate the effective charge on a metal cation in a compound. According to Suchet (1965), the effective charge on a cationic species involved in formation of a chemical bond can empirically be represented by

$$q = n \left[1 - 0.01185 \left(\frac{Z}{r'} + \frac{Z'}{r} \right) \right], \quad (2)$$

where Z , r and n are, respectively the total number of electrons, ionic radius and oxidation number of the cation; and the primed symbols refer to the anion in the compounds. Using the above formula, the effective charge on Mn in MnCl₂, Mn₂O₃ and MnO₂ are calculated and are given in table 1. Similarly, effective charges on Cr in CrCl₃·6H₂O and Cr₂O₃ are calculated using the above method and are given in table 2. It has been observed by other researchers also that the Suchet's formula, given here is not suitable for calculating q when anion radicals, e.g., CO₃²⁻, SO₄²⁻, NO₃⁻, etc are present as ligands to metal ion (Hinge *et al* 2011; Joseph *et al* 2012).

The Pauling's method to estimate effective charge on the other hand, is represented by the following relation (Pauling 1960):

$$q = nI, \quad (3)$$

Table 2. Chemical shift of Chromium K edge and the estimated effective charge on the chromium ions in the compounds.

Compound	Cr ion oxidation state	Chemical shift (ΔE) (eV)	Effective charge (q)	
			Suchet's formula	Pauling's formula
CrCl ₃ ·6H ₂ O	3+	13.73 ± 0.1	1.55	2.25
Cr ₂ O ₃	3+	14.27 ± 0.1	1.87	2.31
Cr ₂ (SO ₄) ₃ *	3+	14.27 ± 0.1	1.87	
Cr(NO ₃) ₃ ·3H ₂ O*	3+	15.69 ± 0.1	2.02	
K ₂ CrO ₄	6+	20.51 ± 0.1		
			Method 1	
			1.01	1.04
			Method 2	
			2.31	1.92
K ₂ Cr ₂ O ₇ *	6+	20.34 ± 0.1	2.31	

*Effective charge calculated from the calibration curve of ΔE vs q .

where n is the valence of the absorbing cation and I the ionicity of the metal–ligand bond calculated as below:

$$I = 1 - \frac{n}{c} \exp \left[-\frac{(X_1 - X_a)^2}{4} \right], \quad (4)$$

where X_1 and X_a are the electronegativities of the ligand and the absorbing atom, respectively and c the coordination number of the absorbing atom. The above expression for ionicity of a partially covalent bond is found to agree with experimentally observed electric dipole moment of many standard molecules. Effective charges on Mn and Cr in the respective binary compounds (without radical as ligands) are also calculated using the Pauling's formula and are shown in tables 1 and 2, respectively.

It should be mentioned here that for finding the effective charges in ternary compounds, viz. CaMnO₃, K₂CrO₄ and K₂Cr₂O₇, no separate formula was suggested by Suchet (1965). However, Ghatikar *et al* (1977) suggested a methodology for finding the effective charge on one of the cations in a ternary compound where effective charges on the cations of the constituent binary compounds (viz. CaO and Mn₂O₃, in case of CaMnO₃) are determined first and the average effective positive charge is distributed on the two cations in the reverse ratio of their electronegativities. Effective charge on Mn in CaMnO₃ was found by the above method (hereafter, referred to as method 1), where the effective charges of the cations in the constituent binaries viz. Mn₂O₃ and CaO, are obtained by both Suchet and Pauling methods and the values are shown in table 1. However, as seen in table 1, effective charges on Mn in CaMnO₃, obtained using method 1, was much less than expected in both the cases for a compound having Mn in Mn⁴⁺ oxidation state and for a chemical shift (ΔE) value of 16.33 eV. The other method (method 2) to find out effective charge on a cation in a ternary compound, also followed by other workers (Chetal *et al* 1988; Pandey *et al* 1990) consider only the 1st coordination shell of the particular cation in the ternary compound. Since in CaMnO₃, Mn has a Mn⁴⁺ oxidation state and an octahedral oxygen

coordination as in MnO₂, effective charge on Mn in CaMnO₃, according to method 2 would be same as that on Mn in MnO₂ and are given in table 1. This value is more realistic than that obtained by method 1, however, since the chemical shift in CaMnO₃ is lower than that found in MnO₂, it appears that method 2 also fails to predict the correct effective charge of Mn in CaMnO₃. Hence, we have opted not to include the effective charge on Mn in CaMnO₃ in generating the calibration curve for ΔE vs V , as discussed below and have obtained the effective charge value from the calibration curve itself.

For finding out effective charge on Cr in K₂CrO₄ by method 1, similarly, we have found out effective charge on K in K₂O and Cr in CrO₃ by both Suchet and Pauling methods and subsequently, the averaging has been carried out as discussed above to find out the effective charge on Cr in K₂CrO₄. However, as seen in table 2, the discussed method has yielded very low value of effective charge on Cr⁶⁺ in K₂CrO₄ and hence cannot be accepted. However, if we consider the 1st coordination shell method (method 2), i.e. tetrahedral coordination of oxygen around Cr as in CrO₃ (Pantelouris *et al* 2004), the effective charge of Cr in K₂CrO₄ appears to be reasonable for Cr⁶⁺ oxidation state, using the Suchet's formula, as shown in table 2. Hence, the above effective charge values on Cr in K₂CrO₄ are taken into account in generating the calibration curve of q vs ΔE in case of Cr compounds as discussed below. However, effective charge on Cr in K₂CrO₄ as obtained using Pauling's formula is still not found to be reasonable even by method 2, as seen in table 2 and hence the calibration curve has not been drawn for Cr compounds using Pauling's formula.

Figures 3 and 4 show plots of measured chemical shift, ΔE , as a function of the calculated effective charge (q) for Mn and Cr compounds. For Mn compounds, effective charges obtained by both Suchet's and Pauling formulae have been plotted in figure 3(a and b), while for Cr compounds, only effective charge obtained from Suchet's formula has been used since Pauling formula possibly yielded wrong result for K₂Cr₂O₇ and K₂CrO₄ samples.

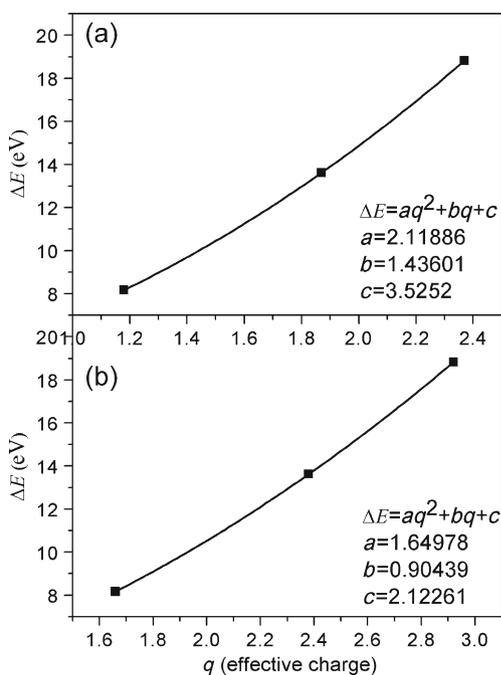


Figure 3. ΔE vs q for Mn compounds with polynomial fit where effective charge is calculated using (a) Suchet's formula and (b) Pauling's formula.

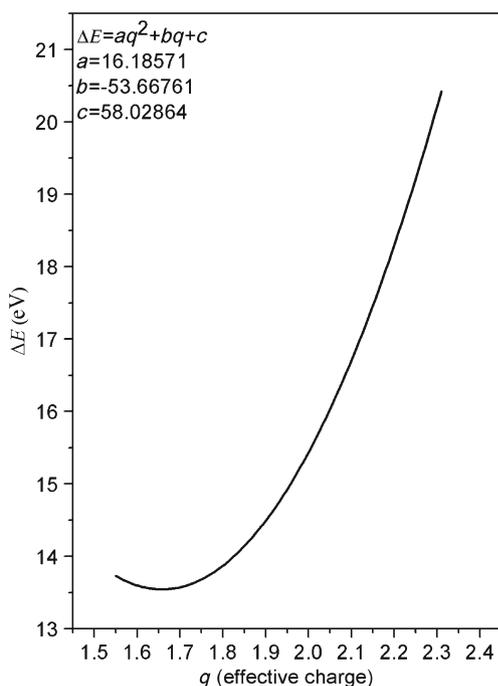


Figure 4. ΔE vs q for Cr compounds with polynomial fit where effective charge is calculated using Suchet's formula.

It has been observed that for both Mn and Cr compounds, the variation of chemical shifts as a function of effective charge can be described by a quadratic equation as follows:

$$\Delta E = aq + bq^2 + c. \quad (5)$$

The best fit values of the parameters a , b and c are given in the corresponding curves. Similar quadratic variation of chemical shift as a function of effective charge has been reported by other researchers also (Kondawar and Mande 1976; Apte and Mande 1981; Chetal *et al* 1988; Pandey *et al* 1990; Hinge *et al* 2011; Joseph *et al* 2012) for compounds of various metal ions. Subsequently, using the above calibration curves and the measured chemical shifts, we have estimated effective charges on metal ions in compounds having radicals viz. Mn ion in MnCO_3 , $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and CaMnO_3 and on Cr ion in $\text{Cr}(\text{SO}_4)_3$, $\text{Cr}_2(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ and $\text{K}_2\text{Cr}_2\text{O}_7$ and the values are listed in tables 1 and 2. The estimated effective charges agree well with that reported by Mande and Apte (1981) for Mn compounds and by Manthiram *et al* (1980) for Cr compounds. As seen in table 2, for Cr compounds, the chemical shift (ΔE) and effective charge (q) have been found to be higher for NO_3 ligand compared to SO_4 ligand for the same oxidation state of Cr, i.e. Cr^{3+} . This agrees with the result obtained by Hinge *et al* (2011) for Cu compounds and is indicative of more ionic nature of the metal- NO_3 bonds compared to metal- SO_4 bonds. Similarly, from table 1, it can be seen that the chemical shift (ΔE) and effective charge (q) have been found to be higher for CO_3 ligand compared to SO_4 ligand for the same oxidation state of Mn, i.e. Mn^{2+} , establishing covalent character of the SO_4 ligand.

4. Conclusions

X-ray absorption spectroscopy measurements were carried out at the Mn K edge around 6539 eV on elemental Mn foil and few Mn compounds viz. MnCl_2 , MnCO_3 , $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, Mn_2O_3 , CaMnO_3 and MnO_2 , where Mn is present in 2^+ , 3^+ and 4^+ oxidation states and with tetrahedral or octahedral coordinations. Similarly, measurements at the Cr K edge were carried out on Cr foil and on a few Cr-containing compounds viz. $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, Cr_2O_3 , $\text{Cr}(\text{SO}_4)_3$, $\text{Cr}_2(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, $\text{K}_2\text{Cr}_2\text{O}_7$ and K_2CrO_4 . Measurements were carried out using the energy dispersive EXAFS beamline at INDUS-2 Synchrotron radiation source at RRCAT, Indore. Energy shifts of ~ 8 – 16 eV were observed for Mn K X-ray absorption edge in the Mn-compounds while shifts of 13 – 20 eV were observed for Cr K edge in Cr compounds compared to their values in elemental Mn and Cr, respectively. The different chemical shifts observed for the compounds having the same oxidation state of the cation but different anions or ligands show the effect of different chemical environments surrounding the cations. The above chemical effect has been quantitatively described by determining the effective charges on Mn and Cr cations in the above compounds. Effective charges were determined analytically using two standard available formulae for compounds having simple anionic ligands and the calibration curves for the chemical shift vs effective charge were generated for both Mn and Cr containing compounds. Using the above calibration curves, effective charges on the cations in compounds having radicals as ligands have been determined.

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